

## Supplementary Information

### Enhancing the energy density and stability of vanadium-based redox flow batteries via a dual active species strategy

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## Experimental Section

### Materials

Vanadyl sulfate ( $\text{VO}_2\text{SO}_4$ , 99%) and cerium carbonate hydrate ( $\text{Ce}_2\text{C}_3\text{O}_9 \cdot x\text{H}_2\text{O}$ , 99.9%) were purchased from Aladdin. Methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ , 99 %) was purchased from Sigma-Aldrich. Sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%) was purchased from Xilong Scientific Co., Ltd. Graphite felts (CF, 5 mm for thickness) was purchased from SCI Materials Hub without further treatment. The Nafion 117 which produced by Dupont was purchased from SCI Materials Hub. Deionized water was supplied by Milli-Q Direct-Q 5UV.

### Preparation of electrolyte

For the V/V-Ce redox flow battery, the positive electrolyte was 10.0 mL solution comprising 1 mol L<sup>-1</sup>  $\text{VO}^{2+}$ , 0.4 M  $\text{Ce}^{3+}$ , 3 mol L<sup>-1</sup>  $\text{CH}_3\text{SO}_3\text{H}$ , and 0.5 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ , and the negative electrolyte consisted of 10.0 mL solution containing 1 mol L<sup>-1</sup>  $\text{V}^{3+}$ , 3 mol L<sup>-1</sup>  $\text{CH}_3\text{SO}_3\text{H}$ , and 0.5 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ . For the all-vanadium flow battery, the positive electrolyte was 10.0 mL solution containing 1.4 mol L<sup>-1</sup>  $\text{VO}^{2+}$ , 3 mol L<sup>-1</sup>  $\text{CH}_3\text{SO}_3\text{H}$ , and 0.5 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ , and the negative electrolyte was 10.0 mL solution containing 1 mol L<sup>-1</sup>  $\text{V}^{3+}$ , 3 mol L<sup>-1</sup>  $\text{CH}_3\text{SO}_3\text{H}$ , and 0.5 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$ .

### Characterization

X-ray photoelectron spectroscopy (XPS) analysis was conducted on an AXIS SUPRA+ spectrometer (Shimadzu/Kratos, Japan) to elucidate the chemical states of the elements. Molecular vibrational spectroscopy was carried out using a Renishaw inVia confocal micro-Raman system (Renishaw plc, UK) equipped with a 532 nm semiconductor laser. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5110) was employed to determine the concentrations of vanadium (V) and cerium (Ce) ions in the anolyte and catholyte before and after cycling.

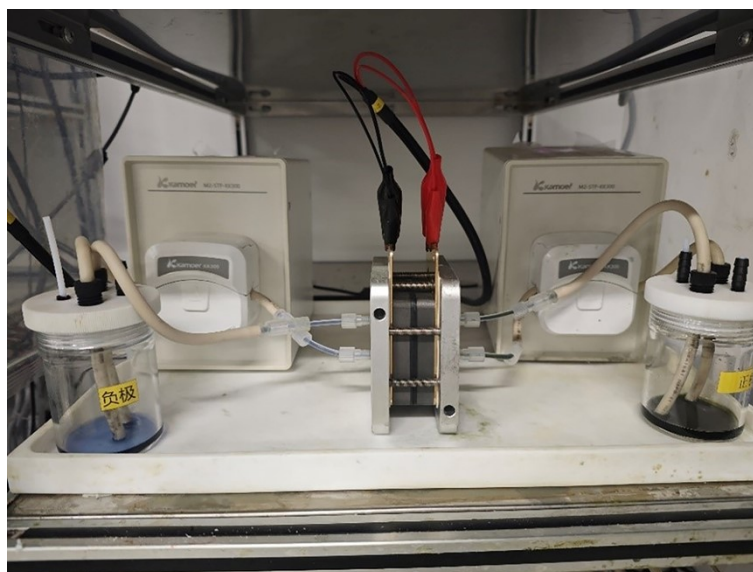
### Electrochemical Test

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted in a three-electrode cell configuration on a VSP BioLogic electrochemical workstation. 10.0 mL solution consisted of 1 mol L<sup>-1</sup>  $\text{VO}^{2+}$ , 0.4 M  $\text{Ce}^{3+}$ , 3 mol L<sup>-1</sup>  $\text{CH}_3\text{SO}_3\text{H}$ , and

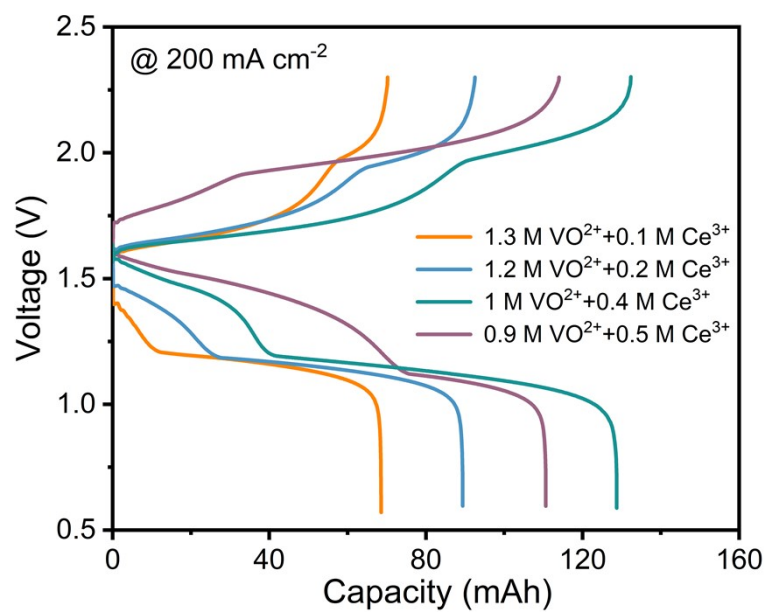
0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, or consisted of 1.4 mol L<sup>-1</sup> VO<sup>2+</sup>, 3 mol L<sup>-1</sup> CH<sub>3</sub>SO<sub>3</sub>H, and 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> were used for positive electrolyte. And the negative electrolyte consisted of 10.0 mL solution containing 1 mol L<sup>-1</sup> V<sup>3+</sup>, 3 mol L<sup>-1</sup> CH<sub>3</sub>SO<sub>3</sub>H, and 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Carbon felt (CF) electrode with dimensions of 1.0 cm × 1.0 cm (geometric area: 1 cm<sup>2</sup>) served as the working electrode, with a platinum mesh served as the counter electrode, and an Ag/AgCl (3 mol L<sup>-1</sup> KCl) electrode as the reference electrode. CV curves were recorded with a scan rate of 0.2 mV s<sup>-1</sup>. The frequency range of EIS was 10<sup>5</sup> to 10<sup>-2</sup> Hz.

### **Flow battery test**

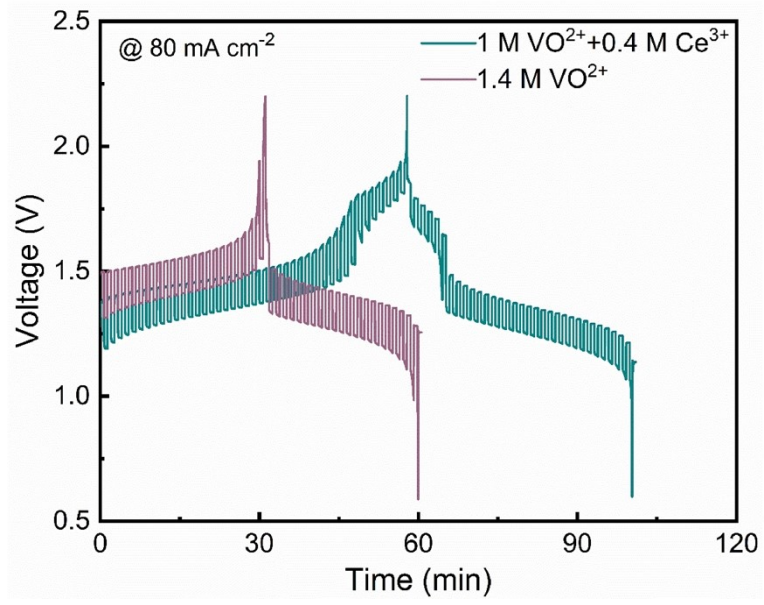
Performance of the redox flow batteries was evaluated using a single-cell test system (LSB-1) manufactured by Wuhan Zhisheng New Energy Co., Ltd. The positive and negative electrodes employed carbon felt (CF) electrodes with an area of 4 cm<sup>2</sup> (2.0 cm × 2.0 cm). Before assembly, the Nafion 117 membrane was soaked in deionized water for more than 24 hours at ambient temperature. A protonated Nafion 117 membrane was used as the separator. The performance of the redox flow batteries was characterized using a LANHE G340A charge-discharge test system, circulated through a peristaltic pump (BT100K) at a flow rate of 150 mL min<sup>-1</sup>. During testing, the charge-discharge voltage window was maintained between 0.6 and 2.2 V. Rate capability was assessed via stepwise current density tests ranging from 40 to 200 mA cm<sup>-2</sup>. At each current density, five consecutive charge-discharge cycles were performed to ensure data reliability, with the performance at 80 mA cm<sup>-2</sup> ultimately being re-tested as a reference. Furthermore, the kinetic characteristics of the electrode reactions were analyzed by the galvanostatic intermittent titration technique (GITT) at 80 mA cm<sup>-2</sup>. Polarization and power density curves were obtained through steady-state polarization tests at a fully charged state (state of charge, SOC = 100%), from which the corresponding power density distributions were calculated.



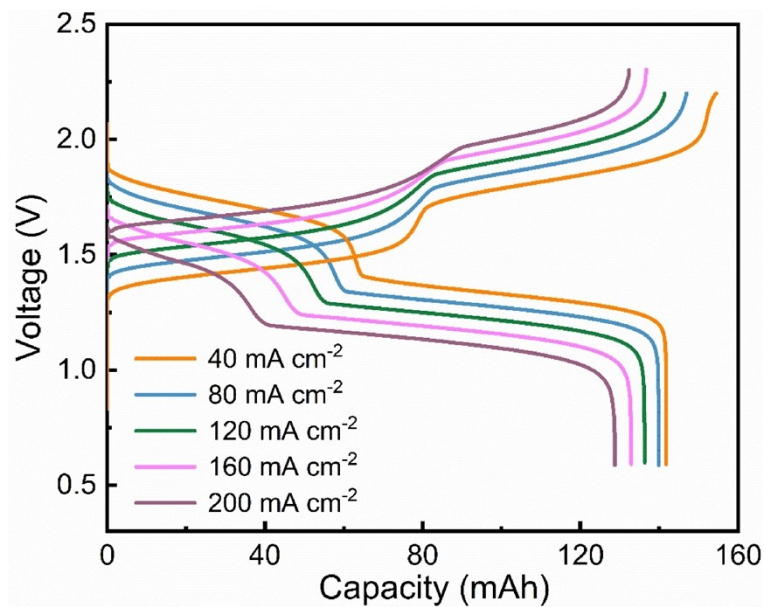
**Fig. S1** Photograph of V/V-Ce RFB.



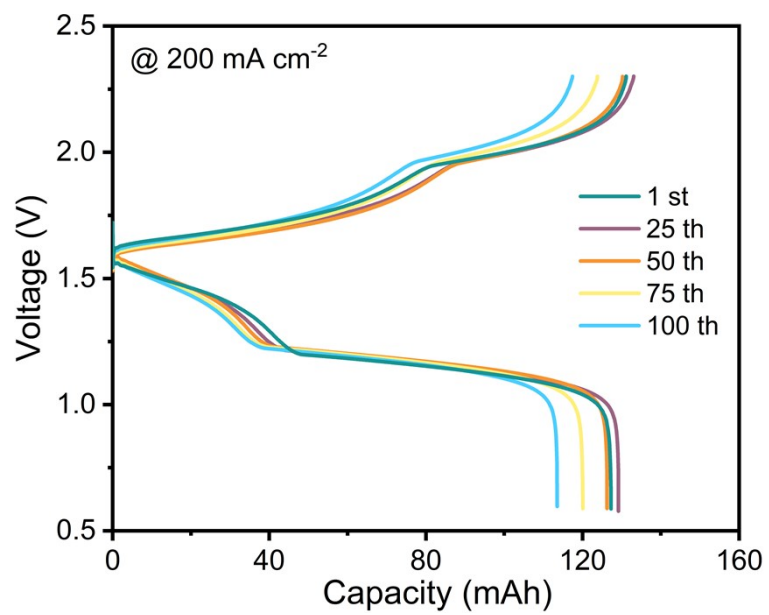
**Fig. S2** Capacity-voltage curve of V/V-Ce RFB with various VO<sup>2+</sup> to Ce<sup>3+</sup> ratios at 200 mA cm<sup>-2</sup>.



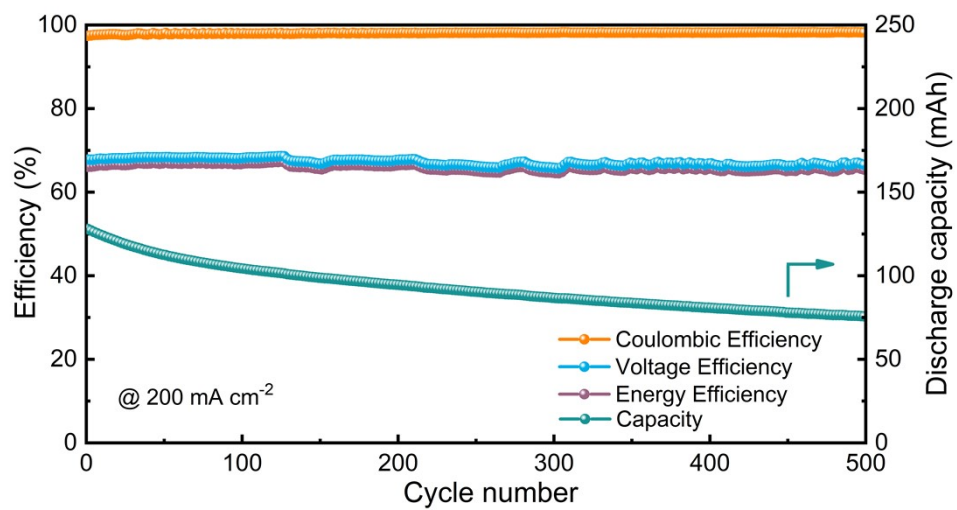
**Fig. S3** GITT profiles of VRFB and V/V-Ce RFB at  $80 \text{ mA cm}^{-2}$ .



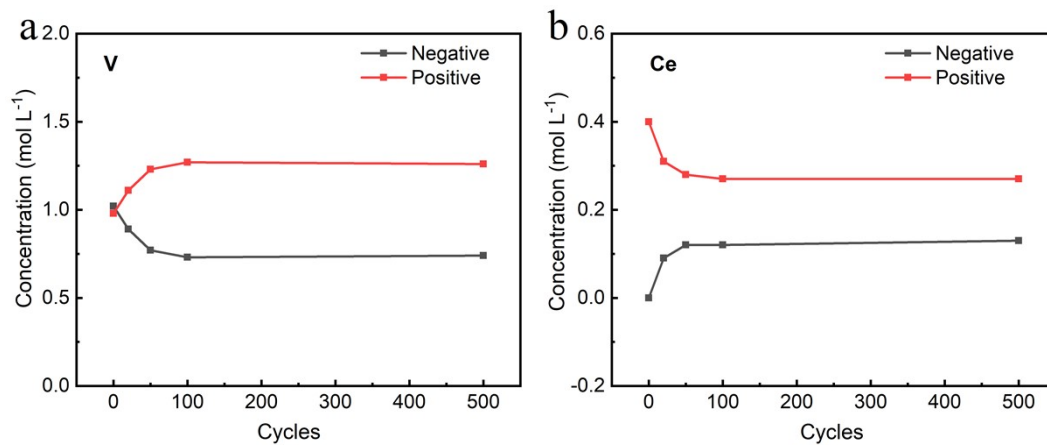
**Fig. S4** Capacity-voltage curves of V/V-Ce RFB at various current densities ranged from 40 to 200 mA cm<sup>-2</sup>.



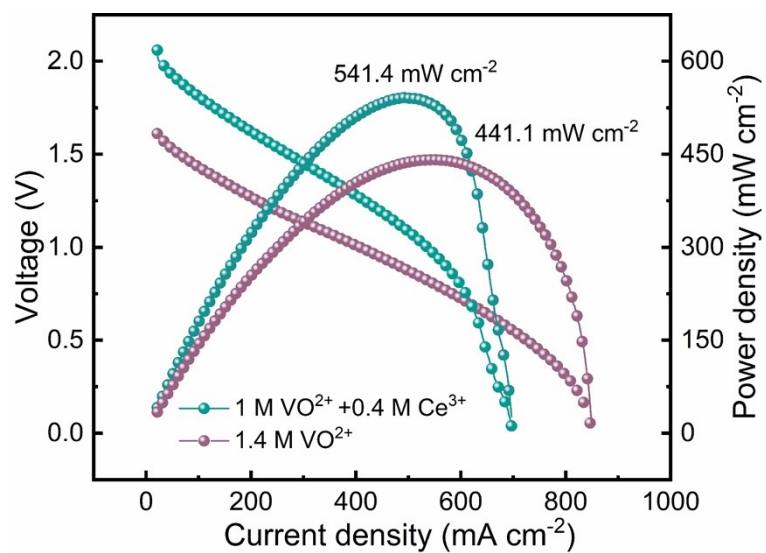
**Fig. S5** The capacity voltage curves at different cycles at  $200 \text{ mA cm}^{-2}$ .



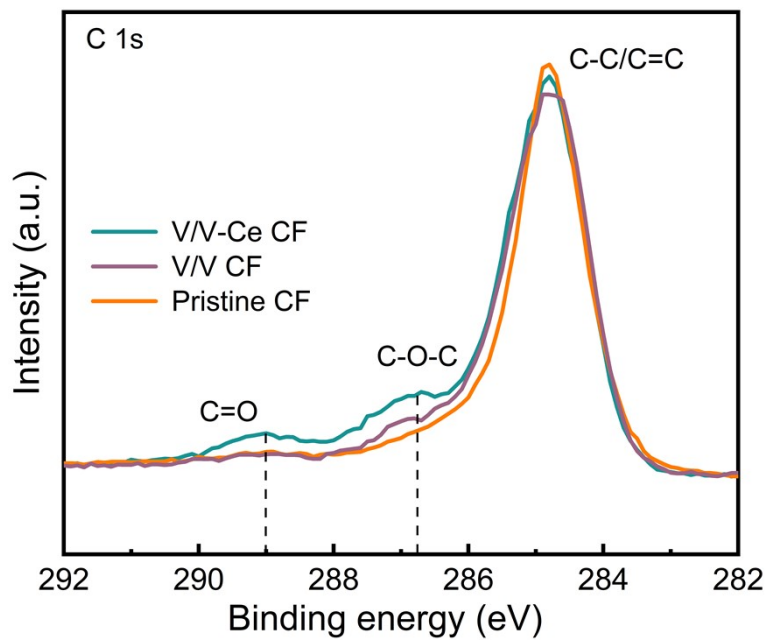
**Fig. S6** V/V-Ce RFB performance at 200 mA cm<sup>-2</sup> within 500 cycles.



**Fig. S7** The evolution of (a) vanadium and (b) cerium concentrations in V/V-Ce RFB based on ICP-OES.



**Fig. S8** Polarization curves and power density for V/V-Ce RFB and VRFB. The negative electrolyte consisted of 10.0 mL solution containing  $1.4 \text{ mol L}^{-1} \text{ V}^{3+}$ ,  $3 \text{ mol L}^{-1} \text{ CH}_3\text{SO}_3\text{H}$ , and  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ .



**Fig. S9** XPS spectrum of the carbon felt electrodes retrieved from the positive side of the V/V-Ce and V/V RFB.

**Table S1.** Economic cost comparison of metals in electrolyte for per kWh of electricity generated.

<b>Parameter</b>	<b>V/V RFB</b>	<b>V/V-Ce RFB</b>
Positive electrolyte composition	1.4 M VO <sup>2+</sup>	1 M VO <sup>2+</sup> + 0.4 M Ce <sup>3+</sup>
Metals required in positive electrolyte for per kWh	9.45 kg VOSO <sub>4</sub>	4.92 kg VOSO <sub>4</sub> + 2.94 kg Ce <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>
Negative electrolyte composition	1 M V <sup>3+</sup>	1 M V <sup>3+</sup>
Metals required in negative electrolyte for per kWh	6.75 kg VOSO <sub>4</sub>	4.92 kg VOSO <sub>4</sub>
Total vanadium cost	\$194.4 / kWh	\$118.1 / kWh
Total cerium cost	\$0 / kWh	\$3.53 / kWh
Total metal cost in electrolyte	\$194.4 / kWh	\$121.6 / kWh

**Table S2.** XPS C1s peak fitting data of positive-side CF in V/V-Ce and V/V RFB, along with pristine CF.

	V/V-Ce		V/V-Ce		Pristine CF	
	Fitted peak area	Ratio (%)	Fitted peak area	Ratio (%)	Fitted peak area	Ratio (%)
<b>C- C/C=C</b>	25747.69	74.80	27009.56	82.90	44091.46	84.90
<b>C-O</b>	6595.52	19.16	2721.52	8.36	4462.40	8.60
<b>C=O</b>	2076.62	6.04	2850.21	8.74	3386.72	6.50